From Petrochemical to Photosynthetic: Algae-Derived Polymers for Sustainable Industrial Applications

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Abstract: The demand for biopolymers made from photosynthetic organisms like algae is growing. This rise is driven by the global shift toward sustainable and renewable resources. This study examines the switch from conventional polymers based on petrochemicals to those derived from algae, emphasizing the potential of the latter for a variety of industrial uses. Algae, including both microalgae and macroalgae, are excellent feedstocks. They can produce various biopolymers such as alginate, carrageenan, agar, ulvan, and polyhydroxyalkanoates (PHAs). Algae grow quickly and do not compete with food crops, making them highly sustainable. Algae-derived biopolymers are useful in many applications, which include food packaging, biomedical devices, pharmaceuticals, and energy storage. Their key properties biodegradability, biocompatibility, film-forming ability, and gelling behaviormake them attractive alternatives. The study also discusses challenges such as scalability, processing methods, and market integration. It reviews the types of algae-based biopolymers, their production techniques, and performance characteristics. Overall, algae-derived polymers ultimately offer a viable route to more environmentally friendly industrial solutions, assisting in the development of a carbon-neutral and circular economy.

Keywords: Algae, Biopolymers, Algal polysaccharides, Polyhydroxyalkanoates, Drug delivery, Energy storage.

1. INTRODUCTION

There are many applications for polymers in our daily lives. These days, sustainability is one of the most significant characteristics of polymers. Actually, just 14% of the plastic used in packaging may be recycled, with the remainder ending up in the environment [1]. A polymer is considered sustainable if it originates from waste, biologically renewable feedstocks, or recycled materials and can rejoin the circular economy's technical or biological loop at the end of its useful life. [2]. Biopolymers are generally considered more environmentally friendly than oil-derived counterparts, despite differences in their propensity to cause global warming and other ecological issues.

Worldwide, algae are a class of photosynthetic aquatic organisms that can be unicellular (microalgae) or multicellular (macroalgae). These organisms are typically divided into three groups of algae: green (Chlorophyta), red (Rhodophyta), and brown (Phaeophyceae). The existence of various forms of chlorophyll and other pigments is the primary distinction between these categories of algae [3]. Algae have also been utilized as a wholesome food source for thousands of years [4], are significant carbon sinks, and drive aquatic food webs and bio-geochemical cycles [5, 6]. Compounds isolated from different kinds of algae have more recently been utilized as the foundation for cutting-edge materials for energy storage, tissue engineering, food packaging, and pharmaceuticals. Natural photosynthetic and en-zy-matic pathways offer promising avenues for the ge-neration of sustainable energy vectors, including elec-trical energy, bio-oil, and hydrogen-rich syngas [7,8].

Severe environmental effects may occasionally result from the growth of algae in water bodies caused by high, excessive nitrogen inputs (eutrophication) [9]. For example, algal respiration causes hypoxic conditions in algal blooms, which may seriously jeopardize aquatic vertebrate survival [10]. However, in contaminated locations, edible macroalgae have been identified as a possible source of heavy metal ingestion [11]. Moreover, antifouling paints are required to preserve the integrity of ship hulls because of hull biofouling with algae species, among other organisms [12]. These paints, however, degrade into tiny particles that have the potential to negatively affect coastal habitats. Given the potentially harmful effects that algae can produce when subjected to human influence, harvesting these organisms sustainably and utilizing their natural components and activities may be an alternative way to lessen those effects while creating environmentally friendly materials and energy sources.

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There have been several advancements in the usage of algae to develop different biopolymer materials in recent years. Numerous methods can be used to extract the naturally occurring cellulose and starch polymers found in algae [13]. Algae are a valuable feedstock source for the synthesis of biopolymers owing to their large number of photosynthetic units. Numerous polymeric classes, including polyesters, polyamides, polyolefins, and others, can be developed by the fermentation of the algae biomass [14]. Algal biomass-based natural polymers have effective antimicrobial, anticancer, antioxidant, and immunomodulatory properties and are less harmful [15,16]. Additionally, biomass from algae can be employed in creating biodegradable composites with enhanced mechanical properties like tensile strength and adhesion [17].

The features and capacity of algal biomass for the production of biopolymers were examined in this review. The techniques to develop biopolymers from algal biomass have been examined. A summary of the various biopolymer types derived from algae ishighlighted, along with instances of their usage in the disciplines of biomedicine, the environment, and energy. Potential opportunities and the need for more research have been emphasized in addition to the thorough evaluation.

2. TYPES OF ALGAE-DERIVED BIOPOLYMERS

A wide range of biopolymers can be produced by algae. Green algae (Chlorophyta), red algae (Rhodophyta), and brown algae (Phaeophyta) are among the many classes into which algae can be divided as different photosynthetic organisms [18,19]. It is possible to extract algal-derived biopolymers from many portions of the algae, including the internal compartments and cell walls. Because of their special qualities, these biopolymers can be used in a wide range of fields, including materials science, biotechnology, food, medicine, pharmaceuticals, and energy. Polyhydroxyalkanoates (PHAs), proteins, and polysaccharides can be produced by microalgae that range in size from 0.02 to 2000 μm [20,21]. Notably, microalgae can provide carbohydrates, which can then be converted into various biopolymers like poly(lactic acid) (PLA) [22]. However, the polysaccharides, such as alginic acid and carrageenan that are used to make bio-based plastics can be produced from macroalgae, often known as seaweed, which range in size from microscopic to 200 ft [23].

2.1. Algal Polysaccharides

Over 70% of the earth's surface is made up of water, and the wide variety of marine life provides a wealth of natural resources, including polysaccharides. Because they are water soluble, biodegradable, and functionally active, they have become a material of interest in biomedical applications. Polysaccharides are abundant in marine algae. These include mucopolysaccharides, storage polysaccharides, and structural polysaccharides found in cell walls [24]. Ulnas, sulfuric acid polysaccharides, xylan, and sulfatedgalactans are the primary polysaccharides found in green algae seaweeds; xylan, carrageenan, fucoidan, water-soluble sulfatedgalactan, porphyran, and mucopolysaccharides are found in red seaweeds [25]; and alginic acid, fucoidan, laminarin, and sargassan are found in brown seaweeds. These polysaccharides are sulfated. Anticoagulant, antiviral, anticancer, and immunoinflammatory properties are among the biological actions of sulfated polysaccharides that are known to exist [24].

2.1.1. Alginate

The cell wall matrix of brown seaweed contains alginates, which are naturally occurring anionic polysaccharides that are members of the linear copolymer (brancheless) family [26]. Alginic acid is the name given to the linear polyuronic acid type. Alginate is a polyelectrolyte and a biopolymer [24]. β-(1,4) linked d-mannuronic acid (Man*Ap* or M) with $^1C_4$ ring conformation and α-(1,4) linked l-guluronic acid (Gul*Ap* or G) with 1C4 ring conformation make up the two monomeric units that make up their primary structure [27] (Figure **1**). About 50% of *Undaria pinnatifida*

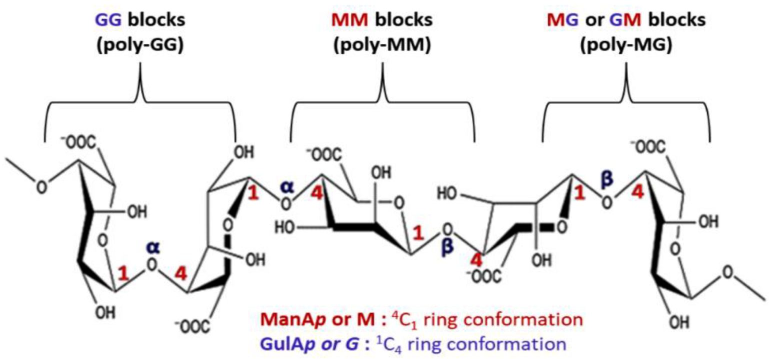

Figure 1: Chemical structure of alginate [27].

contains alginate that has various usage in tissue engineering, medication delivery, and other fields. Alginates and cations can combine to create hydrogels, which offer enhanced recoverability, stiffness, and flexibility. Additionally, it has good adsorption qualities and a high capacity for water retention [28].

According to Yuan and Macquarrie's research, alginate made via extraction had a higher yield (23.13%) than that made by a biorefinery technique [29]. Nonetheless, two different kinds of alginate products with unique qualities were produced by the biorefinery process. The extraction pH affectedthe extraction. Alkaline extraction yielded alginate with excellent extraction efficiency, but extraction at acidic pH resulted in insoluble alginic acids from alginate salts that impededthe extraction [30]. Using multiple-response optimization of the acidic treatment of the brown alga *Ecklonia radiata*, Lobeer *et al*. investigated the sequential extraction of alginate [31]. In their experiment, it was commonly observed that extractability improved under more acidic conditions, particularly at higher temperatures and durations. Accordingly, it was anticipated that an acid treatment at a pH of 2 and a temperature of 45 °C for 110 minutes would resulted in a maximum yield of 39%; however, this was significantly raised to 45% when working at the boundaries of the extended domain with a pH of 1.

2.1.2. Laminarin

Laminarin, also known as laminaran or leucosin, is a naturally occurring polysaccharide that has drawn more attention from researchers worldwide because of its remarkable qualities and variety of uses. The internal storage (cell wall) of brown algae is the primary source of this biodegradable polymer [32]. Particularly, plants in the Laminariaceae family have high levels of it. When it was first identified and isolated in the 19th century, scientists became concerned about its properties and potential uses. These days, a variety of species, such as *Laminaria*, *Saccharina*, and *Eisenia*, contain brown algae that are high in laminarin.

These species are often found throughout Asia and several European nations [33]. On the reducing end, the polymer chains of this polysaccharide are different: the G-type chain ends with d-glucose units, whereas the M-type chain ends with a 1-O-substituted D-Mannitol group (Figure **2**) [34,35]. Algal species and environmental conditions will therefore affect the structure and ratio of these two kinds of laminarin chains, which can impact their bioactivity [36].Laminarin is effectively used in medication delivery, direct ethanol generation, and the marine carbon cycle [37]. The antitumor, antioxidant, and anti-inflammatory qualities are enhanced by oxidation and reduction processes [34]. Purification increased the amount of laminarin with strong antioxidant activity and high anisometric stretching intensity in the Rajauria *et al*. investigation [38].

2.1.3. Fucoidan

Numerous organisms produce fucoidans, which are sulfated water-soluble polysaccharides with a range of biological functions that are relevant to pharmaceuticals. Compared to high molecular fucoidan (HMF), low molecular fucoidan (LMF) has a higher bioavailability [26]. *In vitro*, these substances have anticoagulant [39,40], venous antithrombic [41], and recombinant HIV reverse transcriptase inhibitory potential [42].

Additionally, because they disrupt the molecular mechanisms of cell-to-cell recognition, they can be used to prevent cell invasion by various retroviruses, including HIV, herpes, cytomegalovirus, and African swine fever virus [43]. Additionally, these macromolecules prevent sperm from adhering to the oviductal epithelium and function as anti-angiogenic agents [44]. Algal-sulfated fucoidans also have anticancer and antiproliferative qualities [45]. It is described how these chemicals can be used as functional dietary supplements in addition to their many pharmacological uses [46].

2.1.4. Carrageenan

Among the most prevalent components in the extracellular matrix of carrageenophyte red algae arecarrageenans, which are sulfatedgalactans. These polysaccharides are linear and comprise a repeating disaccharide pattern (carrabiose) made up of either 3,6-anhydro-α-d-galactose (DA-unit) or β-d-galactose (G-unit) (1,4)-linked with an α-d-galactose (d-unit). An α-1,3 glycosidic bond connects the carrabiose units, and the existence or non-existence of the 3,6-anhydro-bridge on the α-d-galactose moiety, as well as variations in the quantity and location of sulfate esters, result in a variety of motifs [47].

In carrageenans, the presence of the 3,6-anhydro-bridge is what propels the creation of the gel. The mature carrabiose motifs are present in the extracellular matrix of carrageenophyte red algae. Industrial applications have taken use of the unique chemical structure and wide range of features that they possess. It is used in medication delivery systems and to avoid membrane fouling [48,49]. A 56% extraction yield was obtained from *K. alvarezii* carrageenan utilizing ultrasound pre-treatment at 90 °C for 15 minutes.

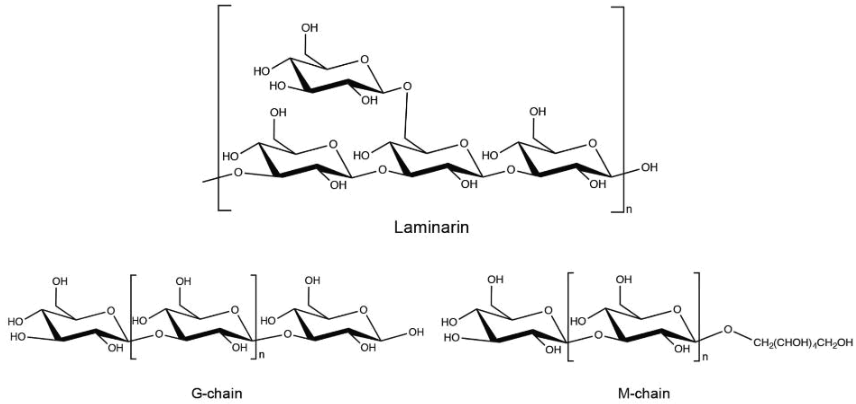

Figure 2: Schematic illustration of laminarin structure [34,35].

The yield of carrageenan is influenced by the extraction method. Carrageenan's molecular weights decrease and there is a small dispersion after extraction [50]. κ-carrageenan has an enhanced viscosity and gel strength. While κ-carrageenan's viscosity solely relies on the temperature of extraction, its gel strength is influenced by its purity, monosaccharide concentration, and critical gel temperature [51].

2.1.5. Ulvan

Green seaweed produces ulvans, which are sulfated polysaccharides that dissolve in water. Numerous physiological and biological actions, including anticoagulant [52], antioxidant [53], antihyperlipidemic [54], antibacterial [55], antiviral [56], anticancer [57], and immunomodulatory qualities [58], have been shown to be evident in them. Rhamnose, xylose, glucuronic acid, iduronic acid, and sulfate groups are basically present in ulvan [59]. The two main repeating disaccharides are type A_3S aldobiuronic acids: β-d-GlcA-(1 → 4) -α -l-Rha3S-(1→) and B_3S: α-l-IdoA-(1 → 4)-α -l-Rha3S-(1→, it can change according to the type of algae, where it is grown, and how it is extracted [60].Ulvan is largely evenly distributed throughout the frond, with the fibrillar wall and intercellular space having the highest concentrations. Figure **3** displays the structural characterization of ulvans that were isolated from *U. papenfussii*[61].

2.2. Poly Hydroxy Alkanoates (PHA)

Microorganism-derived PHA is environmentally friendly and shares characteristics with petrochemical polymers [62]. Stresses brought on by a nitrogen shortage can promote the synthesis of biopolymers. Microalgae like *Synechococcussubsalsus* and *Spirulina* produced novel 14–18 carbon chain PHA biopolymers, but *Chlorella minutissima* did not synthesize PHA biopolymers, even in the presence of nitrogen deficit. Leptolyngbyavaleriana, a microalgal species used to produce PHA, has been shown to have greater thermal stability than other PHAs [20]. The produced bioplastics' glass transition (T_g) and melting temperature (T_m) are between 4 and 10 °C and 79 and 116 °C, respectively [9].

Using non-fastidious microalgal strains such as Botryococcusbraunii, which is thought to have the largest concentration of accumulated PHAs, or media deficient in specific nutrients have been used by some researchers to report increased PHA growth [63].Upscaling of bioprocesses of microalgae–based PHA production is still ongoing and demands a great deal of attention since it is constrained by harvesting, biomass drying, and pretreatment difficulties. To maximize the structure of PHA production plants, Ramos *et al*. proposed a Mixed Integer Nonlinear Programming model [64]. They identified the ideal circumstances for the plant and maximized its net present value. They can also be beneficial to choosing alternatives for biopolymer extraction from cells and in determining the most effective technique for the process.

2.3. Poly Hydroxy Butarate (PHB)

PHB is a biodegradable, apolar, optically active polymer that has garnered a lot of attention due to its comparable qualities to polypropylene [62]. Compared to lignocellulosic biomasses, PHB is formed in greater quantities when a high starch content is present [65]. There are very few published studies that used algae as a precursor in the synthesis of PHB. For their production, a lot of lipid is needed [62]. Low cell growth rates typically result in substantial lipid accumulation for the synthesis of biopolymers. The influence of many elements on PHB formation in *Chorellafusca* was investigated by Cassuriaga *et al*. [62]. As demonstrated by Kavitha *et al*. [66], their study produced the largest amount of PHB (17.4%), exceeding the production in *Botryococcusbraunii*. A PHB content of of 27% was observed after 14 days of growth, which made bioplastic produced from *Chlorella pyrenoidosa* highly biodegradable and environmental

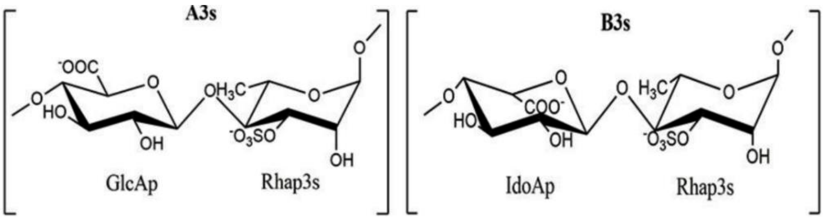

Figure 3: Structural characterization of ulvans extracted from U. papenfussii [61].

friendly [Das67]. The likelihood of generating PHB from agricultural runoff has recently been studied. The full-scale potential of bacterial PHB synthesis was demonstrated, despite the minimal level obtained [68]. Additionally, to create a feasible production method, the accumulation parameters and algae productivity can be optimized.

3. ALGAE-DERIVED BIOPOLYMER PRODUCTION TECHNOLOGIES

Typically, pre-treated macroalgae are used for traditional method of extracting alginate from brown algae. Alkaline extraction, solid/liquid separation, precipitation, drying, and particle size reduction (milling) are then carried out after the pre-extraction with slightly acidic solutions (HCl at low molarity) [69]. But since the ideal extraction procedure has not yet been determined, different extraction variations can be found in both scientific and industrial literature. At the same time, there is an increasing need to create novel, environmentally friendly, and sustainable techniques for extracting biopolymers. In order to enhance sustainability in light of economic feasibility, environmental effect, and process productivity, new technologies and simpler extraction methods have been investigated. Table **1** summarizes the methods of isolation used in the synthesis of biopolymers.

Furthermore, the current lab-scale production methods being investigated are synthetic polymer blends and biopolymers based on microalgae. Compression molding and solvent casting are used to optimize the material properties of the biopolymers by adding compatibilizers, plasticizers, and additives. To create biopolymer, these combinations of synthetic polymers, plasticizer, compatibilizer, additives, and algal-based biopolymer are put into solvent casting and hot compression molds at high temperatures and pressures. According to a study by Khalis, adding 6% Maleic Anhydride (MA) allows for a denser film structure, which improves the surface microstructure's cohesion and smoothness [77].According to Ciapponi *et al.*, adding microalgal biomass as a bio-filler improved the compound's thermal stability under 150 °C and decreased the water contact angle. [78]. However, in DMA testing, the bioplastic formulation containing *Spirulina platensis* and *Chlorella vulgaris* showed a high modulus and a high Tan δ [79]. They also emphasized that lowering the quantity of plasticizer in the mix of algae-based bioplastic can lessen the toughness of the material.

According to research by Sabathini *et al.*, a temperature of 25 °C, and a *Chlorella*:water ratio of 1:5 are ideal for *Chlorella* sonification [80]. Comparing bioplastic film made from chlorella-PVA with and without ultrasonic pre-treatment revealed that ultrasonication can boost the film's elongation % by up to 2.5x and its tensile strength by up to 1.8x. Ultra-sonification can therefore increase the dense uniformity of the film and the binding of PVA and *Chlorella*. A study by Machmud *et al*. demonstrated that the ductility of the material was comparatively decreased when red algae bioplastic was mixed with tropical plant latex [81]. Additionally, *Calostopis gigantea* and *Artocarpus altilis* latex red algae bioplastic were tested for tensile strength. According to the study, bioplastics composed of red algae and latex still had a superior tensile strength than those manufactured of starch. Table **2** summarizes the processes for producing biopolymer blended film generated from algae

3. TYPICAL APPLICATIONS OF ALGAE-DERIVED POLYMERS

Algal-derived polymers are appealing alternatives to conventional synthetic materials because of their unique functional properties, biodegradability, and renewability. These biopolymers, which are derived from both microalgae and macroalgae, have good gelling, thickening, and film-forming qualities. They include alginate, carrageenan, agar, and ulvan. Their varied uses offer sustainable solutions in a variety of industries, including food packaging, energy, pharmaceuticals, agriculture, and biomedical engineering.

3.1. Biomedical Applications

Important characteristics of biopolymers are their high tensile strength, water-holding capacity, biodegradability, and non-toxicity. Because of these distinctive properties, biopolymers are an excellent feedstock for the biomedical engineering industry, particularly in the fields of regenerative medicine and bone-tissue engineering. Because of their

Table 1: Methods of Isolation Used in the Synthesis of Biopolymers

Isolation technique	Procedure	Processing conditions	Advantages	Ref.
Solvent extraction	Algal biomass is grown and combined with the chosen chemical solvent in a suitable ratio. The mixture is agitated at room or elevated temperature (30–60 °C) for several hours followed by filtration or centrifugation to separate the solid residue from the solvent-containing extract.	Temp.= 32-180°C pH= 5.5-8.7 Time= 10-300 min	Easier Less downstream processing compared to fermentation	[68,70,71]
Microwave-assisted extraction	Algal powder is mixed with the appropriate solvent and then transferred to a microwave extraction. Microwave radiation is then applied under controlled conditions.	Temp.= 150 °C Time= 3 min	Fast and consistent Compact process Brief experimental durations Minimal solvent consumption No energy needs	[62]
Ultrasound-assisted extraction	Ultrasound-induced cavitation produces turbulence, which causes collisions and agitation of the microparticles in the biomass of algae. Algal cell walls are disrupted as a result of the conversion of ultrasonic energy into vibrational energy. The ultrasound effect increases the rate of transfer, which makes it easier to extract biopolymers from algal biomass.	Temp.= 25 °C Time= 30 min	Significant reduction in extraction times. The yield is unaffected when extraction is done at room temperature. Processes for membrane separation are not necessary. Prevents material losses. Eco-friendly	[72]
Pressurized liquid extraction	The process involves applying high pressures and temperatures to the solvent (below its critical point) in order to maintain its liquid state. High temperatures and pressures can increase solubility, which improves the solvent's ability to penetrate the matrix and extract the desired chemicals.	Temp.= 20-200 °C Time= 5-15 min Pressure= 1-20 MPa	Increased extraction efficiency with tiny volumes of solvents Brief extraction duration Increased mass transfer rate	[73,74]
Enzyme-assisted extraction	The enzymes used in EAE are safe for use in large-scale processes since they are non-toxic, food-grade, and ecologically benign. Cellulases and proteases, the main enzymes employed, efficiently compromise the integrity of the algal cell wall.	Temp.= 50-65 °C pH= 2-4.5	Increased extraction efficiency Reduced use of solvents Lower energy usage Brief extraction period	[75,76]

Table 2: The Process for Producing Biopolymer Blended Film Generated From Algae is Summarized By Microalgae-Polymer Blends

Production technology	Microalgae strain	Polymer blend	Optimum condition used	Ref.
Hot compression mold	*C. vulgaris*	PVA	Plasticizer: Glycerol Compatibilizer: MA 2% - 6% Compatibilizer Initiator: Dimethyl Sulfoxide (DMSO) 15 mL Dimension of mold: 100 × 200mm Moldingtemp.: 120 °C	[77]
	S. platensis	Biobased wheat gluten polymer	Plasticizer: glycerol, octanoic acids and 1,4-butanediol Thickness of mold: 0.1 cm Molding temp.: 120 °C Pressure: 4000 kPa	[78]
	Chlorella and Spirulina	PE polymer	Plasticizer: glycerol, octanoic acids and 1,4-butanediol Molding temp.: 150 °C	[79]
Solvent casting	*Chlorella*	PVA	Casting temperature: 80 °C Casting geometry: 150 × 150mm	[80]
Handmade blended sheet	*Eucheuma Conttonii*	Latex: *Artocarpus altilis and Calostropis gigantea*	Mold geometry: 21 × 29.7 cm Drying technique: Open air drying	[81]

biocompatibility and adjustable biodegradability, biopolymers are widely used in bone and cartilage TE. Some of the most widely utilized biopolymers for bone tissue engineering are PLA and PLGA polyesters. For example, a gas foaming technique has been used to create PLA and PLA-calciumphosphate scaffolds, which have been implanted *in vivo* to promote bone regeneration [82].

3.1.1. Hydrogel Scaffolds

Human adipose derived stem cells (hASCs) were transduced by Jin *et al*. [83] using a replication-deficient adenovirus that carried hTGF b2 (Ad5-hTGF b2). Following transduction, the cells were planted and grown in PLGA/alginate compounds. The chondrogenic potential of hASCs makes them a possible origin of seeded cells for cartilage tissue engineering. Fucoidan's anticoagulant, antiviral, and immunomodulatory properties give it a variety of biological uses. Fucoidan was added to electrospun PCL to create a unique biopolymer material for bone regeneration [84]. Additionally, ulvan/PDLLA and ulvan/PCL scaffolds for medication administration, wound care materials, and bone TE were reported [85]. Nowadays, developing biodegradable scaffolds for cardiac TE is a challenging undertaking. A graft comacromer comprising alginate and polypropylene fumarate (PPF) was used to construct biosynthetic amphiphilic hybrid hydrogels, including monomodal network hydrogel (HPAS-NO) and bimodal network hydrogel (HPAS-AA) (Figure **4**) [86].

The HPAS-AA hydrogel degraded gradually *in vitro* in PBS (phosphate buffered saline), but it was more durable in the culture medium than HPAS-NO. Because of its nanoporous nature, the HPAS-AA absorbed both free and structured water. Even after 18 days, the HPAS-AA hydrogel was cytocompatible and promoted the 3D cell development of H9C2 cardiomyoblasts and L929 fibroblasts. Structured water's ability to respond to cells is what gives HPAS-AA hydrogel its superior and resilient cellular growth.As a result, cardiac TE may benefit greatly from HPAS-AA hydrogel. Thankam and Muthu [87] copolymerized poly(mannitol fumarate-co-sebacate) (pFMSA) with alginate (ALG) to create a hybrid comacromer. By crosslinking pFMSA with Ca^{2+} and vinyl monomers acrylic acid (AA), bimodal hydrogel pFMSA-AA was created. Because of its physiochemical and biological favorability, AA is appropriate for cardiac TE.

3.1.2. Drug Delivery

The lack of an effective carrier system has hindered the delivery of proteins, peptides, and antigens in the creation of new generation vaccines. A novel vaccine's formulation must take into account a number of factors, including stability in the host, toxicity, budgetary considerations, and the capacity to elicit a suitable and sustained immune response. Recent years have seen the development of biodegradable polymer microcapsules and microspheres for the controlled release of various pharmaceutical agents and macromolecules. These devices enable the constant discharge of encapsulated antigen and effectively deliver them intracellularly to produce humoral and cellular immunity [88]. Silymarin-loaded PLGA nanoparticles (NPs) were encapsulated by El-Sherbiny *et al*. [89] in alginate-based pH-responsive hydrogels, allowing for a prolonged release of the

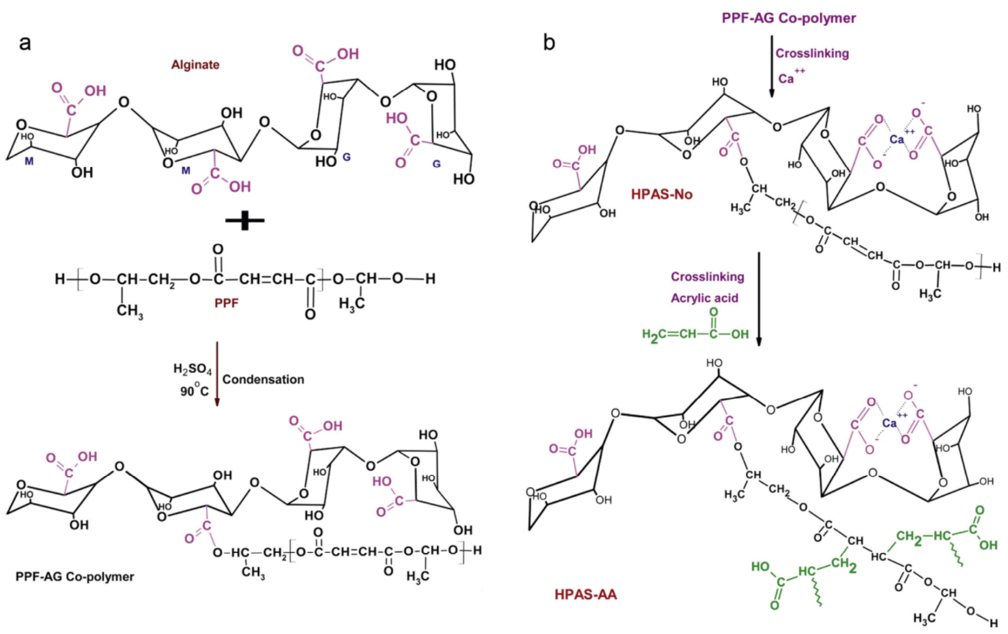

Figure 4: (**a**) Hydrogel monomodal network synthesis and PPF-ALG graft comacromer synthesis (HPAS-NO), and (**b**) bimodal network hydrogel (HPAS-AA) [86].

silymarin, mostly in the intestinal area. The milk thistle is used to extract silymarin, a mixture of three flavonolignans (silybin, silychristin, and silydianin) that exhibit antioxidant action, stimulate protein synthesis, support cell regeneration, and prevent the development of cancer [90,91].

Among the primary reasons for illness and mortality worldwide is heart failure, especially myocardial infarction. Thrombosis, incomplete durability, and re-operation are some of the limitations of surgery, one of the recognized therapy options for myocardial infarction [92]. To treat myocardial infarction, numerous biological methods have been employed, such as TE and medication delivery. In one study [93], transcriptional activator (TAT), which is produced from the HIV virus, was combined with heat shock protein 27 (HSP27) to increase its ability to pass through cell membranes. TAT-HSP27 was released under control using an alginate hydrogel-based delivery method and a PLGA microsphere loaded with TAT-HSP27.

3.2. Battery Energy Storage Systems

Liedel's definition of thegreen battery cycle, as depicted in Figure **5**, should ideally be terminated when batteries are made using biopolymers derived from natural sources [94]. This cycle involves the production of biomass from photosynthesis in plants, such as algae, which is then biologically prepared to creategreenbatteries that generate energy and repurpose their CO_2 emissions for photosynthesis. All of the necessary battery components, including electrodes (in raw or carbonized form), binders, electrolytes, and separators, can be made from biomass obtained from algae and other natural sources. Nonetheless, the majority of algal biopolymers are employed as separators and electrolytes.

Alginates and cellulose are common materials utilized as separators, but a number of other algal biopolymers have also been studied as ion-conducting membranes [95]. Li metal batteries use separators made of poly(ethylene oxide) (PEO) and sodium alginate. Poly(ethylene oxide) absorbs the liquid carbonate electrolyte, allowing Li ions to diffuse, while sodium alginate sustains the film's structure [96]. By incorporating nano-sized fibers from the naturally occurring mineral attapulgite with sodium alginate, Song *et al*. produced a green porous separator with strong heat and chemical resistance. In a Li-ion battery, the liquid electrolyte might be efficiently wetted into this separator [97]. A renewable separator with enhanced ionic conductivity (5.8 mS/cm) and strong cycling qualities in Li-ion batteries was created by blending soy protein with algal cellulose, which was derived from food industry algae waste [98]. The investigators highlighted their separator membranes' high porosity of 80–90% as compared to pure soy protein separators, their good mechanical qualities, and the fact that the average pore size relied on the proportion of the cellulose derived from algae. The membranes were also heat stable up to 150 °C.

For energy storage devices, such as batteries, the majority of research focuses on employing algal biopolymers as solid polymer electrolytes. By creating a matrix with various ionic dopants, like Li or Mg salts, the biopolymer in these devices combines the roles of an electrolyte and a separator [99]. Alginate and κ-carrageenan are examples of polysaccharides, which are popular algal biopolymers used in electrolyte membranes or hygrogels [100,101]. Although κ-carrageenan is already utilized on a somewhat significant scale in a variety of sectors, its hydrophilic and low mechanical properties make it difficult to use as a polymer electrolyte [102].However, it is frequently

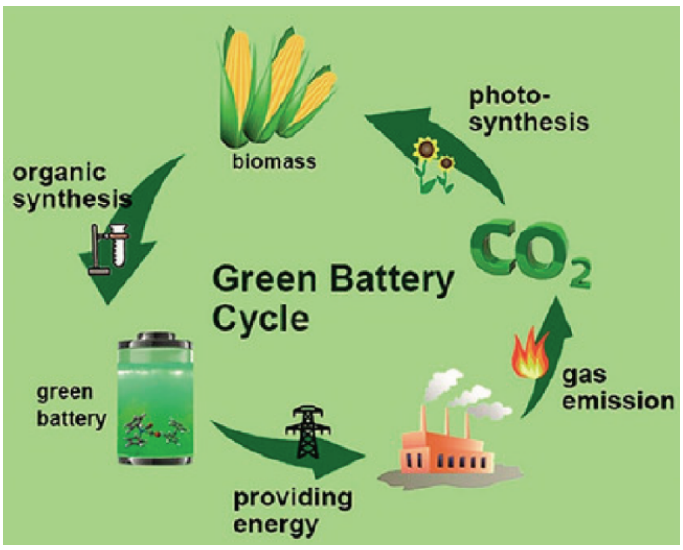

Figure 5: Green battery cycle by Liedel [94].

researched for many battery kinds. Arockia Mary and colleagues employed κ-carrageenan in Li-ion batteries, adding $LiNO_3$ to the biopolymer to boost ionic conductivity and achieved electrochemical stability of up to 3.2 V for the ideal concentration of $LiNO_3$ [103].

When Rudati *et al*. introducedNH_4Cl to κ-carrageenan, the detached film that was produced was used as an electrolyte in an organic C/Zn battery that produced a voltage of 2.1 V [104]. Nithya *et al*. doped κ-carrageenan with ammonium bromide to produce an electrolyte with a high conductivity of 2.8×10^{-3} S/cm. An open-circuit voltage of 4.29 V was shown by the battery having this electrolyte, a zinc/graphite anode, and a lead oxide/graphite/vanadium pentaoxide cathode [105]. By doping sodium alginate with sodium thiocyanate (NaSCN), Diana *et al*. created alginate electrolytes and created an all-solid-state sodium-ion battery [106]. For usage in magnesium-ion batteries, magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) was inserted in sodium alginate; this produced an ionic conductivity of 4.6×10^{-3} S/cm and an open-circuit voltage of 1.93 V [107]. By creating a mixture of alginate/chitosan and reinforcing the mixture with $ZnCl_2$, Fernández-Benito *et al*. produced an aqueous zinc ion polyelectrolyte with a conductivity of approximately 10^{-3} S/cm and a high electrochemical cyclability of over 7000 cycles. [108]

The limited ionic conductivity of native algal biopolymers restricts their direct application in high-performance energy systems. More so, long-term performance and safety issues are raised by the possibility of algae-derived materials degrading under high voltage or during extended cycling. Future studies will concentrate on modifying the chemical makeup of biopolymers generated from algae to improve their ionic conductivity, electrochemical stability, and suitability for use with battery electrodes and electrolytes. Combining conductive elements like graphene, carbon nanotubes, or metal oxides with algae-based biopolymers to create sophisticated solid electrolytes, binders, and separator membranes for next-generation batteries. These polymers are highly suited for flexible batteries used in wearable and transitory electronics due to their film-forming and biodegradable properties. Biodegradable battery components for low-impact disposal may be investigated in future research.

3.3. Food Industry

Alginate is a crucial polysaccharide that finds a wide range of uses in industries such as food, medicine, cosmetics, and textiles, which has resulted in a notable 20% growth in its market share [109,110]. When added to food, alginate can enhance its physicochemical characteristics and structure. This polysaccharide has been used as a gelling agent, setting agent, emulsifier, stabilizing agent, suspending agent, and food drying prevention [110]. Additionally, it can lower production costs and boost industrial economic efficiency. Alginate has been utilized as an edible film and coating for fresh foods to lower lipid oxidation, limit microbial contamination, and improve the food's water vapor barrier (preventing dehydration). As a result, alginate coatings have helped to increase the shelf life of commodities like fruits [111], vegetables [112], and meat [113]. In order to create a potent antioxidant, Gopu and Selvam [114] used ultrasound to extract the algae strain *Amphiroa rigida*. The produced ARPS was found to have strong antioxidant properties because it can scavenge DPPH and ABTS.

3.4. Biofuels

Bioethanol, biomethane, biodiesel, biohydrogen, and biogas are examples of liquid, gaseous, or solid biofuels that can be produced from algae biomass[115]. Algal polysaccharides, primarily from brown algae, are fermented or gasified to make bioethanol with a substantial amount of carbohydrates but also from green and red algae [116]. Green and blue microalgae are particularly intriguing for the production of biofuel as biopolymers should typically be present in high concentrations in bioenergy feedstock. Cellulose is a type of biopolymer that, with the right pretreatment of the cellulose feedstock, can be utilized to produce biofuel by simultaneous saccharification and fermentation or co-fermentation [117]. The algal biomass must undergo pretreatment to break down its cell walls and release the intracellular biopolymers [118]. Both enzyme-mediated and biological agent-mediated biological pretreatment are possible.

Therefore, it is advantageous to combine the manufacturing high-value goods or wastewater cleanup with the production of biofuel from algae. As shown in Figure **6** [119], algal oil was extracted in a biorefinery idea put out by Arun *et al*. from *C. vulgaris* biomass for biodiesel production and the PHB biopolymer from the de-oiled cake. Das *et al*. [67] reported using *Chlorella pyrenoidosa* to produce PHB and biofuel together. AlMomani *et al*. examined the effects of various pretreatments, including enzymatic, acidic, and microwave laser-hydrogen peroxide-Fe-nanoparticle pretreatment, on the synthesis of bioethanol and biopolymer from algal biomass [120]. Kumar *et al*., however, focused on the de-oiled algal biomass that had been subjected to a hybrid physicochemical/enzymatic pretreatment and discovered that it could be utilized as a feedstock for the production of both bioethanol and biopolymer

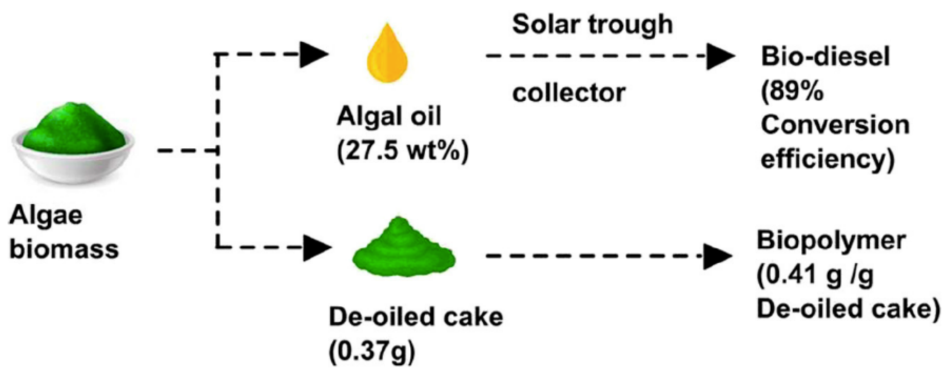

Figure 6: Simultaneous synthesis of the biopolymer PHB from the de-oiled cake and algal oil for biodiesel [119].

(PHB); as a result, the entire quantity of de-oiled algal biomass could be utilized efficiently and without generating waste [121].

3.5. Other Applications

Strong and efficient adsorption is produced when biological molecules are used in adsorption, and no secondary pollution results. Furthermore, it is easily recovered and repurposed [122]. Color removal and heavy metal remediation are accomplished by an adsorption technique that combines clays and biopolymers. Biopolymers like polysaccharides and polypeptides are used since natural clays are unable to remove hydrophobic pollutants. This produces a blend that is effective for cleaning up the environment [123]. Documenting the mechanical and biological properties of naturally occurring bio-based materials is now a challenge in the extensive research of biopolymers for 3D printing technologies [124]. In their PVA biocomposite for 3D printing, Ponthier *et al*. used the algae Nannochloropsis salina as a filler [125]. Biopolymers are versatile enough to be employed in a wide range of applications where distinct material qualities are required.

CONCLUDING REMARKS AND PROSPECTS

The current desire to replace fuel-based polymer sources essentially lays the groundwork for converting algae into an effective material for the manufacture of biopolymers. The application of algae as a possible source of biopolymers and the synthesis of biopolymers derived from algae can both thrive at an extraordinary level with the availability of various research findings. A sink for the biologically sequestered CO_2 into the necessary biopolymer production may be made possible by the introduction of the "top-down" strategy, which will be extremely advantageous for both environmental and economic reasons. This review's goal is to present the relevance of algal biomass and its future possibilities for biopolymer manufacture. Furthermore, attention has been drawn to current advances in the techniques for creating biopolymers from algal biomass and their applications in industry. Although the development of biopolymers generated from algae has advanced significantly, there are still a number of research gaps that need to be filled in order to fully utilize these materials in commercial settings. First, in order to lower production costs while preserving a constant level of biomass quality, large-scale culture systems for both macroalgae and microalgae need to be optimized. Second, the absence of defined extraction and purification procedures for biopolymers including PHAs, ulvan, carrageenan, and alginate results in variations in the performance and characteristics of the materials. Third, little is known about the structure–property correlations of these polymers, especially when they are used in specific applications such as energy storage systems, packaging, or biomedical devices.Furthermore, when compared to petrochemical alternatives, the environmental impact of producing polymers from algae is not well quantified by life cycle assessment (LCA) data. Finally, integrating algae-derived biopolymers into existing supply chains and guaranteeing their compatibility with present production infrastructure remain key difficulties. To speed up the commercial acceptance of algae-based polymer solutions, these gaps must be filled by interdisciplinary cooperation, cutting-edge processing techniques, and pilot-scale demonstrations.

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